Synthesis and characterization of templated pentaborate(1-) salts: X-ray structure of [(2-HOCH2CH2)C4H7NMeH][B5O6(OH)4]·0.3H2O

Jones, Charlotte; Beckett, Michael; Coles, Simon J.; Davies, Richard; Horton, Peter N.

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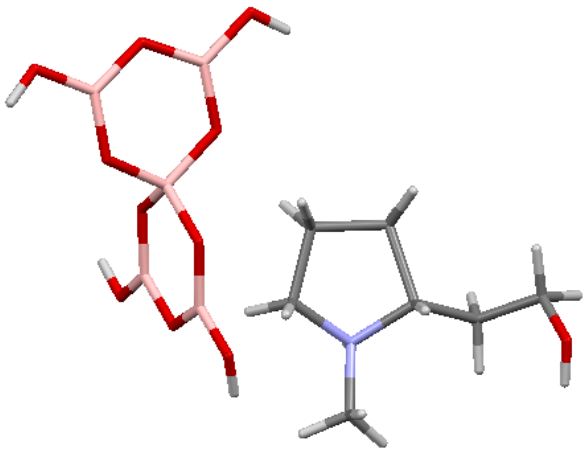
Synthesis and characterization of templated pentaborate(1-) salts: X-ray structure of $[(2\text{-}HOCH_2CH_2)C_4H_7NMeH][B_5O_6(OH)_4]\cdot 0.3H_2O$

Charlotte L. Jones,[1] Michael A. Beckett*,[1] Simon J. Coles,[2] R. Andrew Davies,[1] Peter N. Horton.[2]

[1]*School of Chemistry, Bangor University, Bangor, Gwynedd, LL57 2UW, UK*

[2]*School of Chemistry, University of Southampton, Southampton, SO17 1BJ, UK*

GRAPHICAL ABSTRACT



Abstract *The synthesis of pyrrolidinium pentaborate(1-) and four substituted pyrrolidinium pentaborate(1-) salts from $B(OH)_3$ in aqueous solution are salts are reported. Characterization (IR, NMR, single-crystal XRD) of $[(2\text{-}HOCH_2CH_2)C_4H_7NH_2][B_5O_6(OH)_4]0.3H_2O$ is described in detail. The cation is the largest of the five pyrrolidinium cations studied. A consequence of this is that its solid-state structure has anion-anion interactions ($\alpha\alpha\alpha\gamma$) which are different from the other four ($\alpha\alpha\alpha\beta$) structures. There are also stabilizing cation-anion H-bond interactions.*

Keywords Pentaborate(1-); H-bonds; Pyrrolidinium; X-ray structure; Oxidoborate

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Address correspondence to Dr M.A. Beckett, School of Chemistry, Bangor University, Bangor, Gwynedd, UK.
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INTRODUCTION

Pentaborate(1-) salts, $[NMC][B_5O_6(OH)_4]$, are often prepared from the reaction of organic bases with $B(OH)_3$ in aqueous solution, where the protonated organic base is a non-metal cation (NMC).[1] Occasionally, salts containing rarer anions e.g. three to fifteen B atoms, have also been obtained.[2-9] In basic aqueous solutions, $B(OH)_3$ forms a dynamic combinatorial library (DCL) of polyborate anions whose concentrations are pH and boron concentration dependent.[10-11] Recently, we noted from DFT calculations (gas-phase)[12] on the relative stabilities of the polyborate anions that the pentaborate(1-) anion is not the most stable and yet despite this, $[NMC][B_5O_6(OH)_4]$ salts are readily formed. Strong anion-anion H-bond interactions are present in $[NMC][B_5O_6(OH)_4]$ salts and these we believe are responsible for their facile formation. Herein, we report the synthesis of several pentaborate(1-) salts partnered with substituted pyrrolidinium cations, explore steric effects of the cation, and describe in detail the synthesis of the salt $[(2\text{-}HOCH_2CH_2)C_4H_7NMeH][B_5O_6(OH)_4]$ (**1**).

RESULTS AND DISCUSSION

Synthesis and characterization

The pyrrolidinium pentaborate salts $[(2\text{-}HOCH_2CH_2)C_4H_7NMeH][B_5O_6(OH)_4]0.3H_2O$ (**1**), $[(2\text{-}HOCH_2)C_4H_7NH_2][B_5O_6(OH)_4]0.5H_2O$ (**2**), $[C_4H_8NMeH][B_5O_6(OH)_4]0.5CH_3COCH_3$ (**3**), $[C_4H_8NMe_2][B_5O_6(OH)_4]$ (**4**), and $[C_4H_8NH_2][B_5O_6(OH)_4]$ (**5**), were all prepared in high yields from the reaction of the free base (**1**-**3**, **5**), or quaternary amine hydroxide salt (**4**), with $B(OH)_3$ in a 1:5 molar ratio. Characterization data including single-crystal XRD structural analyses for salts **2**-**5** have been recently been reported elsewhere.[13]

Characterization data[14] (IR, NMR) obtained for **1** were in agreement with those previously reported for related pyrrolidinium and other non-metal cation pentaborate salts. ^1H and ^{13}C NMR spectra (obtained in D_2O) were fully consistent with those expected for the cation, with the NH, OH and BOH protons overlapping and represented by a broad singlet at ~4.7 ppm due to rapid exchange. Three characteristic signals at ~17, 13 and 1 ppm were observed in ^{11}B NMR spectra, obtained in concentrated aqueous solutions (D_2O), which are assigned to $B(OH)_3/[B(OH)_4]^-$, $[B_3O_3(OH)_4]^-$ and the 4-coordinate centre of $[B_5O_6(OH)_4]^-$, respectively.[15] These species are

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observed due to the complex borate equilibria observed in aqueous solution.[11,16] The IR spectrum of **1** clearly shows the diagnostic band[16] of pentaborate salts at ~925 cm^{-1}.

X-ray structure of [(2-$HOCH_2CH_2$)C_4H_7NMeH][$B_5O_6(OH)_4$]

The crystallographic data for compound **1** is given in a footnote[17] with full details given in the supplementary data.[18] The ionic salt is comprised of the expected (2-hydroxyethyl)-*N*-methyl-pyrrolidinium(1+) cation, partnered with a pentaborate(1-) anion, as shown in Figure 1. The cation was found to be disordered over multiple sites with three significant positions of occupancy identified (4:3:3 ratio) and one of which also included a solvated water molecule. All the disordered versions of the pyrrolidinium ring have an envelope conformation with both substituents equatorial. The bond lengths and internuclear angles observed within the boroxyl (B_3O_3) rings of the pentaborate anions of **1** are within the ranges observed for previously reported [NMC][$B_5O_6(OH)_4$] structures.[1,6,15,16] The bond lengths and internuclear angles also lie within the ranges found in related boroxole (B_3O_3) structures containing both 3- and 4-coordinate B centres bound to O.[19]

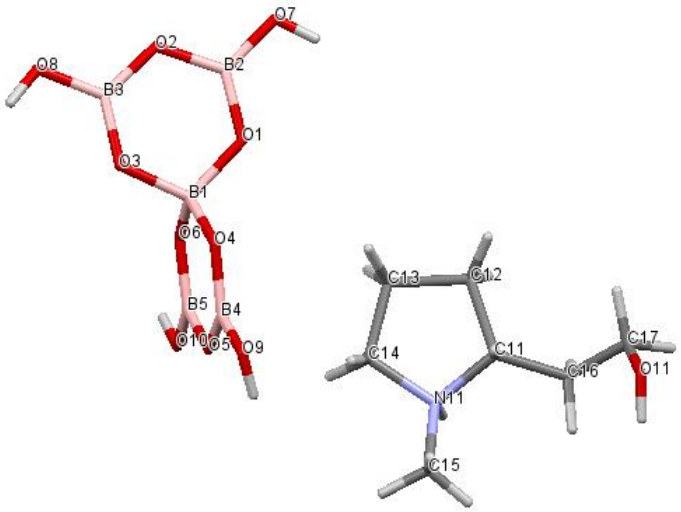

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Figure 1 The structure of [(2-$HOCH_2CH_2$)-C_4H_7NMeH][$B_5O_6(OH)_4$] (**1**), showing the atomic numbering scheme.

Structure **1** possesses a giant H-bonded anionic lattice, with the substituted pyrrolidinium cations (and the H_2O) sitting within the cavities of the lattice. The anions arrange themselves in a series of 'planes' (Figure 2) H-bonded together *via* $R_2^2(8)$ reciprocal pair interactions[21] to ααγ acceptor sites, and the 'planes are linked through further reciprocal-α $R_2^2(8)$ interactions.

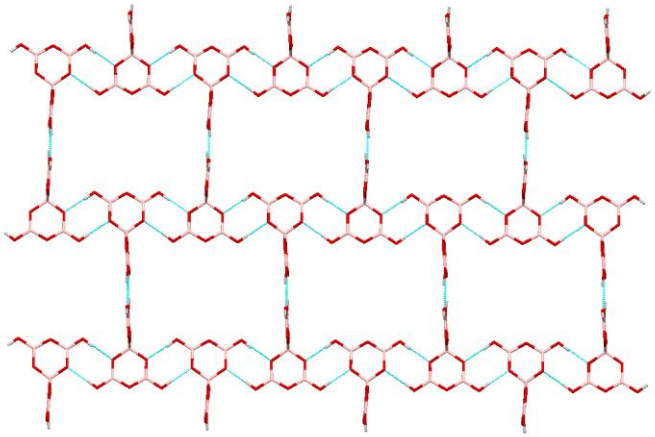

Figure 2 Anionic lattice of **1** viewed along the *a* axis; the [(2-$HOCH_2CH_2$)C_4H_7NMeH]$^+$ cations sit H-bonded within the cavities of the lattice. The $R_2^2(8)$ reciprocal-α H-bond interactions are shown in blue.

The anions of the H-bonded lattice are in a different arrangement to that observed for **3**-**5** that have a familiar αααβ 'brickwall' structure.[1,15] It is interesting to compare the structures of compounds **1** with **4** and **5**. The brickwall structure is sufficiently flexible to accommodate cations of variable sizes (within limits). *e.g*. the *N*,*N*-dimethylated pyrrolidinium cation in **4** has the same structure as the unsubstituted cation in **5**, despite a formula unit increase in volume of 13.3%.[13] The formula unit volume of **1** has increased by a further 10.3% compared to **4**, as a consequence of the larger substituted cation. This, we believe, is responsible for switching the structure from the brickwall to the αααγ arrangement. In this structure three strong reciprocal-

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α bonds (-21 kJ mol^{-1}) are maintained and the H-bond energy for a reciprocal-γ interaction is the same as that of a C(8) β-chain (-16 kJ mol^{-1}).[13] The cation in **1** is also 'non-innocent' and cation-anion H-bond interactions *e.g.* N11H11…O4', N11H11…O9', and O11H11B…O8', further stabilize the self-assembled crystal structure. Full details are available in the supplementary information.

SUMMARY

The synthesis and crystal structures of pyrrolidinium pentaborate(1-) and 4 substituted pyrrolidinium pentaborates are reported. The larger cation present in **1** is unable to fit into the brickwall structure and as a result **1** adopts a similar but different anionic lattice of comparable energy. The solid-state structure of **1** is further stabilized by cation-anion H-bond interactions.

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14. Characterization data for **1**: $C_7H_{20.60}B_5NO_{11.30}$. Elem. Anal Calc: C, 23.8; H 5.9; N, 4.0. Found: C, 23.8; H 5.7; N, 3.9%. Mp >300 ^oC. IR (KBr/cm^{-1}): 3399(br,s), 2973(m), 2893(m), 1639(m), 1432(m), 1315(s), 1100(s), 1027(s), 923(vs), 776(s) 707(s). NMR (400 MHz, D_2O) δ^1H/ppm: 3.82-3.76 1H (m), 3.72-3.61 2H (m), 3.46-3.38 1H (m), 3.18-3.12 1H (q, 8 Hz) 2.90 3H (s), 2.41-2.32 1H (m), 2.19-2.01 3H (m), 1.86-1.76 2H (m). δ^{11}B/ppm: 16.8, 13.2, 1.2. δ^{13}C/ppm: 66.8 (CH), 58.2 (CH_2), 55.9 (CH_2), 38.9 (CH_3), 32.0 (CH_2), 28.8 (CH_2), 21.1 (CH_2).
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17. A *Rigaku AFC12* goniometer equipped with an enhanced sensitivity (HG) *Saturn724+* detector mounted at the window of an *FR-E+ SuperBright* molybdenum rotating anode generator with VHF *Varimax* optics (70μm focus) was used. X-ray data for **1**: $C_7H_{20.60}B_5NO_{11.30}$, M = 353.69; monoclinic space group *P*21/*c*, *a* = 10.0014(7) Å, *b* = 11.4193(8) Å, *c* = 14.8649(10) Å, α = 90°, β = 104.6400(10)°, γ = 90°; *U* = 1642.6(2)Å^3; *Z* = 4; *T* = 100(2) K; Wavelength = 0.71075 Å; density (calc) = 1.430 Mg/m^3; Absorption coefficient 0.125 mm^{-1}; Crystal: colourless prism, 0.110 x 0.100 x 0.080 mm^3; *F(000)* 740; θ range for data collection 3.073 - 27.484°; Index ranges $-12 \le h \le 12$, $-14 \le k \le 14$, $-19 \le l \le 18$; 22146 reflections collected with 3746 independent reflections [R_{int} = 0.0321]; Completeness to θ = 25.242°: 99.7%; absorption correction: semi-empirical from equivalents; refinement method: full-matrix least squares on F^2; data/restraints/parameters 3746/244/261; goodness-of-fit on F^2, 1.103; Final *R* indices [$F^2 > 2\sigma(F^2)$] *R1* = 0.0787, *wR2* = 0.2322; *R* indices (all data) *R1* = 0.0944, *wR2* = 0.2484; extinction coefficient n/a; largest diff. peak and hole 0.743 and -0.509 e Å^{-3}.
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